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ORIGINAL ARTICLE

Red-oils in ethylene plants: formation mechanisms, structure and emulsifying properties

Fabrice Cuoq[1] · Jérôme Vachon[1] · Jan Jordens[2] · Gerard Kwakkenbos[2]

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Abstract In most ethylene plants, the caustic sections suffer from red-oils formation which results from the polyaldol condensation of some oxygenate species in basic media. These red-oils lead to solid material deposition which is generically referred to as fouling and which can cause severe energy losses or operational issues. This specific red-oil fouling can be successfully mitigated by regularly washing the caustic scrubber with a hydrocarbon washing stream which acts as a solvent. However, such washing streams can be further rerouted to the quench water system, increasing the risk of emulsion formation due to its amphiphilic components, i.e., red-oils, compromising the safe operation of the whole plant. The complexity of red-oil structures renders its analysis and characterization challenging. Consequently, there has been no study showing the effect of the type of hydrocarbon wash on the red-oils structure and its potential emulsifying properties. This study describes an in-house developed analytical technique based on UPLC-High resolution QTOF which allows characterizing hydrocarbon streams with complex mixtures of oxygenated species. This method has been successfully applied to monitor red-oil structures during a plant trial where Pyrolysis Gasoline and Toluene-Xylene hydrocarbon washes were successively applied. The data revealed that reactive compounds from the Pyrolysis Gasoline react with the polyaldol species, likely through a Diels–Alder mechanism, thus increasing the diene adduct concentration in the red-oil. It was further found that toluene-xylene washes hindered the emulsifying properties of the red-oils more effectively than Pyrolysis Gasoline washes, in that they could best inhibit the formation of polyaldols adducts.

Keywords Caustic tower · Red-oil · Quench water · Gasoline · TX-cut · Aldol condensation · Fouling · Emulsifier · UPLC-Q-TOF

Introduction

Caustic towers of ethylene plants are usually located upstream of the last stage of the cracked gas compressor. Cracked gas is contaminated with acid gases (e.g., H_2S and CO_2) as well as "low oxygenates" (e.g., formaldehyde, acetaldehyde and propionaldehyde). H_2S (originating from sulfur containing species in the feedstock) and CO_2 (originating from coking/decoking reactions in the furnace) can poison catalysts and degrade the quality of the final product. Such contaminants are thus removed by caustic scrubbing, which consists in circulating a weak sodium hydroxide solution ($\sim$1 wt%) in one part of the column and a strong sodium hydroxide solution (5–10 wt%) in the other part of the column.

At alkaline pH, aldehydes (present at concentrations of hundreds ppm) can react through an aldol condensation reaction, thus leading to oligomerisation or polymerisation fouling. This solid fouling can cause severe energy losses or operational issues. This type of fouling is known as "red-oil", the color originating from the amount of conjugated double bounds in the structures (Fig. 1, compound of type **1**) [7].

✉ Fabrice Cuoq
Fabrice.Cuoq@SABIC.com

[1] SABIC T&I, STC Geleen, P.O Box 319, 6160 AH Geleen, The Netherlands

[2] DSM Resolve, Urmonderbaan 22, 6167 RD Geleen, The Netherlands

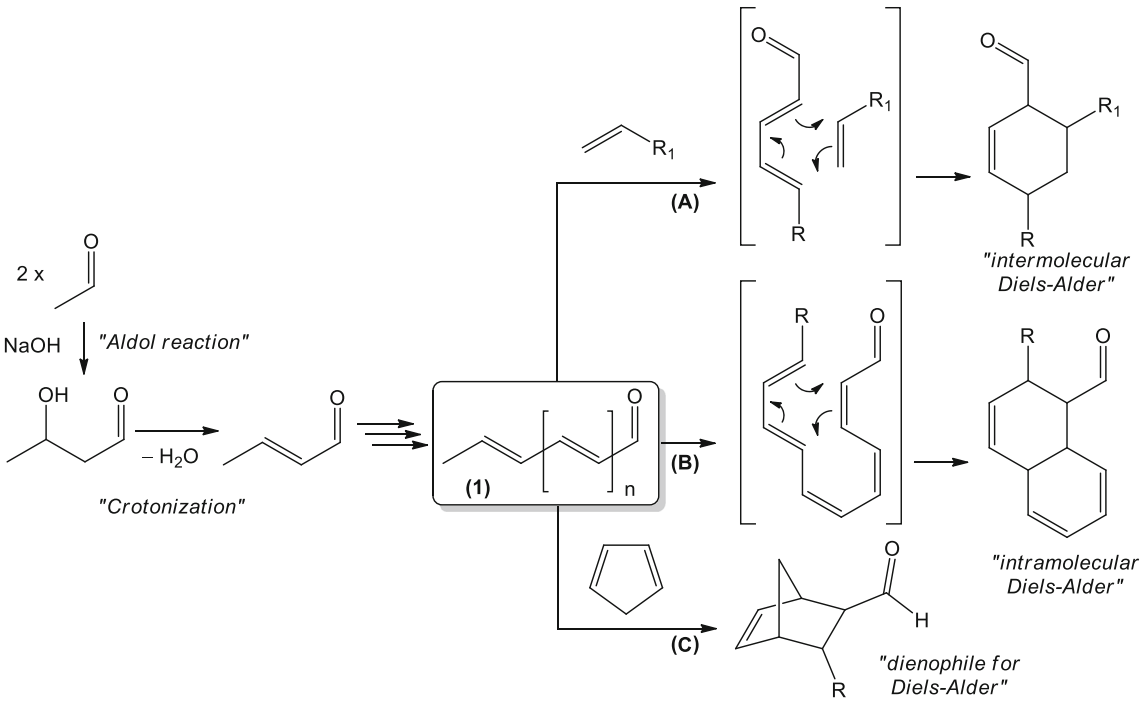

Fig. 1 Generation of aldol polymer from acetaldehyde in the presence of caustic leading to red-oil formation and subsequent Diels–Alder reactions involving polyaldol species with, *A* intramolecular reaction, *B* intermolecular reaction (*R* repetitive methyl-vinyl group, R_1 aliphatic hydrocarbon) and *C* Diels–Alder with cyclopentadiene

Due to the presence of diene functionalities in the polyaldol condensates, one can expect these species to further undergo reactions through intermolecular (Fig. 1, pathway A) and intramolecular (Fig. 1, pathway B) Diels–Alder mechanisms. The polyaldol condensate might also further react with other α,β-unsaturated aldehydes or unsaturated hydrocarbons from the cracked gas such as cyclopentadiene forming branching and cyclic structures which lead to a very complex mixture of oxygenated species [8, 10]. Moreover, when R_1 (=aliphatic hydrocarbon chain) is relatively small (*e.g.,* compound **1** where $n = 1$), the polyaldol condensate might rapidly react with other dienes such as cyclopentadiene (Fig. 1, pathway C) [5, 6]. However, and besides the well-known red-oils structures of type **1**, there has been no experimental proof of the alteration of red-oils with other species through pathway A and C, the reason being the high complexity of such structures.

In spite of the rather low operating temperatures (room temperature to ~40 °C in the tower and 'downstream' spent caustic system), it has also been claimed that radical polymerization can occur [3]. It is recognized that the large species formed from radical polymerization can deposit onto tower internals, causing major operating problems.

Two common methods can be used to mitigate red-oil from formation and accumulation: (1) carbonyl traps to reduce the rate of aldol formation [2]; and (2) aromatic solvent washes [1, 4]. Carbonyl traps are often effective in reducing the rate of aldol condensation and in removing aldols through the caustic purges, but they do not suppress the Diels–Alder type oligomerization mechanism. Additional use of dispersants on top of the carbonyl trapping agent (and even a radical scavenger) are thus often proposed by chemical vendors to cover all possible mechanisms, leading to costly treatments [9]. Within our company, the "aromatic solvent washes" option proved to be a very efficient and cheap alternative and was achieved by rerouting a plant stream containing high amounts of aromatic compounds with low unsaturated hydrocarbons content (e.g., a Toluene–Xylene cut: "TX-cut"). This aromatic wash acts as a solvent, which efficiently displaces the oligomeric red-oils from the water phase into the aromatic phase avoiding their further oligomerization and precipitation. Since aromatic solvents are often of commercial value in the industry, a cheaper gasoline stream, i.e. pyrolysis gasoline (PyGas) from the quench water tower (QWT) of the plant, was used instead. This stream contains a high amount of reactive compounds (about of 7 % of indene, styrene, cyclopentadiene,…), which might have the potential of enhancing the mass of red-oil type of fouling through pathways A or C shown in Fig. 1.

Additionally, the wash streams containing the red-oils exiting the caustic section of an ethylene plant are usually rerouted to the QWT at a rate of few tons per hour. The QWT of an ethylene plant is aimed at quenching the

cracked gas with water to remove heavier compounds from the main stream before it reaches the compressor section of the ethylene plant. Two phases are therefore present in the bottom of such tower, i.e., process water (PW) and PyGas. A global process scheme is described in Fig. 2. Due to the similarity of red-oil structures with surfactants (long a-polar chain and polar head), it can be expected that some emulsions can be formed [11]. Emulsions are undesired in such section as they will lead to carry over of organics to sections that are specifically designed to run with water only. Emulsions will lead to fouling formation and throughput issues. However, to the best of our knowledge, there is no information on (1) how the red-oils are altered from the reactive species present in the PyGas and (2) if these new red-oils possess enhanced water/Pygas emulsifying properties.

To study such influence, a plant trial using a nonreactive aromatic wash (i.e., TX-cut) as aromatic wash for the caustic tower was then performed to probe the effect of red-oil structures on emulsion stability in the QWT. Quality of the red-oil during this trial was monitored using a method newly developed in-house for the complex analysis of red-oil species using UPLC-QTOF. This method allows to qualitatively estimate the amount of species with respect to the number of Oxygen vs Carbon atoms, or Oxygen vs Double Bond Equivalent (DBE). DBE is a value corresponding to the amount of double bonds and ring structures a molecule possesses. This paper thus describes (1) this newly developed analytical technique, (2) the water/PyGas emulsifying properties of red-oils originating from PyGas and TX-cut washes and (3) their respective structural analysis in terms of oxygen vs carbons atoms and DBE.

Materials

The investigated caustic section comprises a caustic scrubber followed by a settling vessel that allows the separation of the red-oil and the spent caustic. The red-oil stream is then rerouted to the QWT at a rate of few tons per hour. The red-oils were sampled in the red-oil settler (see Fig. 2).

PW and PyGas were taken from the QWT bottom to assess the demulsification capacity of the system.

Methods

Hydrocarbon wash

PyGas wash was performed by injecting the PyGas from the bottom of the QWT in the feed of the caustic scrubber, sample A was sampled from the red-oil settler after a month of such treatment. The TX-cut wash was performed by injecting TX-cut directly at the feed of the caustic scrubber, samples B, C, D were sampled from the red-oil settler after 2, 15 and 30 days of TX-cut wash. All samples were compared to each other visually and using UPLC-QTOF as described below.

Red-oil analysis

Samples were analyzed with UPLC-QTOF (Bruker MaXis HD) using electrospray ionization in positive and negative ion mode (results obtained in negative mode are not shown here as no acids were measured in our samples). Automatic peak extraction was performed using the Extract Molecular

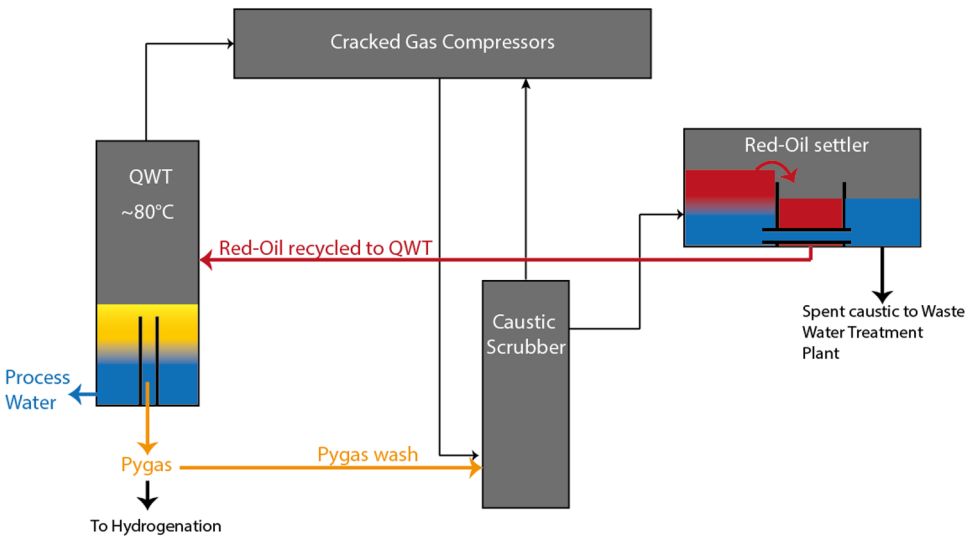

Fig. 2 Generic process scheme describing interaction between quench water tower and caustic section

Feature^{TM} algorithm. The extracted accurate masses were identified with the restriction that only CHO is used, including sodium adducts. Unidentified peaks were thereafter removed from the obtained peak list. The identified compound list was further cleaned by removing unnatural elemental combinations using parameters: O/C ratio <0.75 (e.g. PEG = 0.5) and DBE/C ratio also <0.75 (e.g. benzene = 0.66). Finally, the peak list retrieved from the blank THF sample was subtracted from the resulting peak list. The extensive set of elemental compositions was not identified individually due to the very high amount of hits. Therefore, for plotting, the intensity of the peaks was used, which could not be recalculated towards a concentration. Because of the high variation in compounds type and corresponding response factors, proper quantification is still a point of research. The results are visualized in a contour plot where either the DBE or the #C is plotted against the #O.

Demulsification experiments

Demulsification experiments were conducted using PW with PyGas above atmospheric pressure (0.5 bar overpressure) and at ~80 °C. Such experiments consist in mixing both phases (1000 rpm) for approximately 5 min. 60 mL of each phase is added into a double glass reactor that can sustain overpressure up to 2 bars. The glass reactor is closed with a septum to allow pressure build-up during heating to 80 °C with circulating oil (through the double glass wall of the reactor). Stirring is performed with a magnetic stirrer. After 5 min, the stirring is stopped and the time required to separate water from oil is subsequently recorded (which is called "full demulsification" time). After full demulsification, the turbidity of the water phase is then measured at room temperature which gives an indication of its organic content. The red-oil is added prior mixing at 80 °C with a syringe through the septum. Turbidity measurements were performed using a turbidity meter TN100CAL from Thermo Scientific Eutech.

Results and discussion

Red-oils from PyGas wash and its influence on PyGas/PW separation

In the current plant configuration, the red-oil recycle to the QWT is small relative to the total feed of the column (<1 %). To test if red-oils could act as emulsifiers at such low concentrations, "PW/PyGas" (from the QWT) demulsification experiments with 0.1, 0.4, and 2 % of red-oils (issued from the PyGas wash containing unsaturated hydrocarbons in the caustic tower) were thus performed—the results are shown in Table 1.

No particular effect of the red-oils on the demulsification times, even at 2 % concentration, was observed. However, after full demulsification, a significant increase in the turbidity values for the vessels containing red-oils was noticed (up to 26 % increase), even at low red-oils concentration. Since the separate addition of 2 % red-oils to an isolated water phase does not lead to a turbidity increase, this effect can only be explained by an enhanced emulsification phenomenon. The role of red-oils in enhancing the emulsion phenomenon was thus proven. The plant trial using TX-cut instead of PyGas as aromatic wash was thus performed to evaluate if the emulsifying effect of the red-oils could be minimized.

Red-oils from TX-cut wash: plant trial

A visual observation of the red-oil samples before and during the trial was performed. The number of consecutive conjugated double bonds affects the color of the samples, with a higher number of consecutive conjugated double bonds leading to a darker color [7].

As shown in Fig. 3, lighter colors are observed when the TX-cut wash is performed (B–C and D) vs the aromatic wash with PyGas (A). Based on this difference in color, it is speculated that TX-cut does not react further with the polyaldol species and thus does not increase the molecular weight further like the PyGas wash does. Analysis by UPLC-QTOF was performed on these samples to confirm this visual observation. The contour plots obtained with our in-house technique allows a better understanding of the complexity of the red-oils structures from each sample while offering a clear readability (Fig. 4).

As can be seen in the contour lots of O vs C in Fig. 4, the first sample (sample A—caustic tower treated with PyGas) contains a very high amount (dark red zone) of molecules having about 5–7 oxygens and 10–25 carbons. Similar high concentrations are observed in the contour plot of O vs DBE and correspond to the area of about 5–7 oxygens and 0–15 DBE. Thus, sample A contains a significant amount of small aromatic/conjugated oxygenates.

These small aromatic/conjugated oxygenates are not present in the samples issued from the treatment with TX-cut as can be seen with the absence of this large dark red zone in samples B, C and D. Because of the low operating temperature of the caustic scrubber (i.e., 40 °C) and the low molecular weight of the species identified in sample A, it is speculated that PyGas enhances the amount of red-oil oligomers, most probably from monomeric species from the PyGas (e.g., indene) which can react through a Diels–Alder mechanism with the aldol oligomers to form these

Table 1 Results of demulsification with PW/PyGas and red-oils addition (from PyGas wash)

	Blank	Red-oil 0.1 %	Red-oil 0.4 %	Red-oil 2 %
Full demulsification time (s)	25 ± 4	24 ± 6	27 ± 3	27 ± 3
pH	8.3 ± 0.2	8.2 ± 0.1	8.1 ± 0.2	7.8 ± 0.3
Turbidity (NTU)	259 ± 10	337 ± 6	320 ± 12	350 ± 10
% Increase turbidity	–	23 %	19 %	26 %

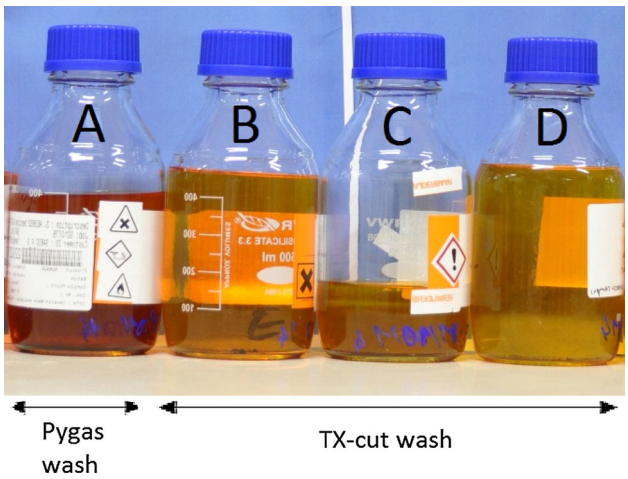

Fig. 3 Pictures of the red-oil samples during the trial. Sample *A*: red-oil after 1 month of operating with PyGas wash; Sample *B*: red-oil after 2 days of TX-cut wash; Sample *C*: red-oil after 15 days of TX-cut wash; Sample *D*: red-oil after 30 days of TX-cut wash

aromatic/conjugated oxygenates; red-oil oligomers being highly reactive dienophile due to the presence of oxygen next to the double bond.

The global intensity of the contour plots of the samples during the TX-cut wash is also lower than for the contour plot obtained of the samples treated with PyGas. The oxygen-containing compounds are present at a lower level during the TX-cut trial, indicating less potential fouling and possibly less emulsification capacity. Indeed, oxygen-containing compounds are more polar and have a higher tendency to stabilize oil in water emulsion.

Red-oils influence on Pygas/PW separation (from PyGas and TX-cut wash)

A comparison on the emulsifying property of the red-oil during the TX-cut wash (1 month after switching) with the red-oil during the PyGas wash was performed. Since demulsification times were not affected as seen previously, only the water turbidities after addition of 1.5 vol % of red-oil were recorded—the results are shown in Table 2.

Results indicate that a higher turbidity is reached for the vessel containing the red-oil from PyGas wash compared with the vessel containing the red-oil from the TX-cut wash with 20 % increase vs 9 % increase, respectively. These experiments show that the quality of the red-oil is positively affected by the change to a TX-cut wash which lowers its emulsifying properties. However, one should keep in mind that red-oils can be only one of the

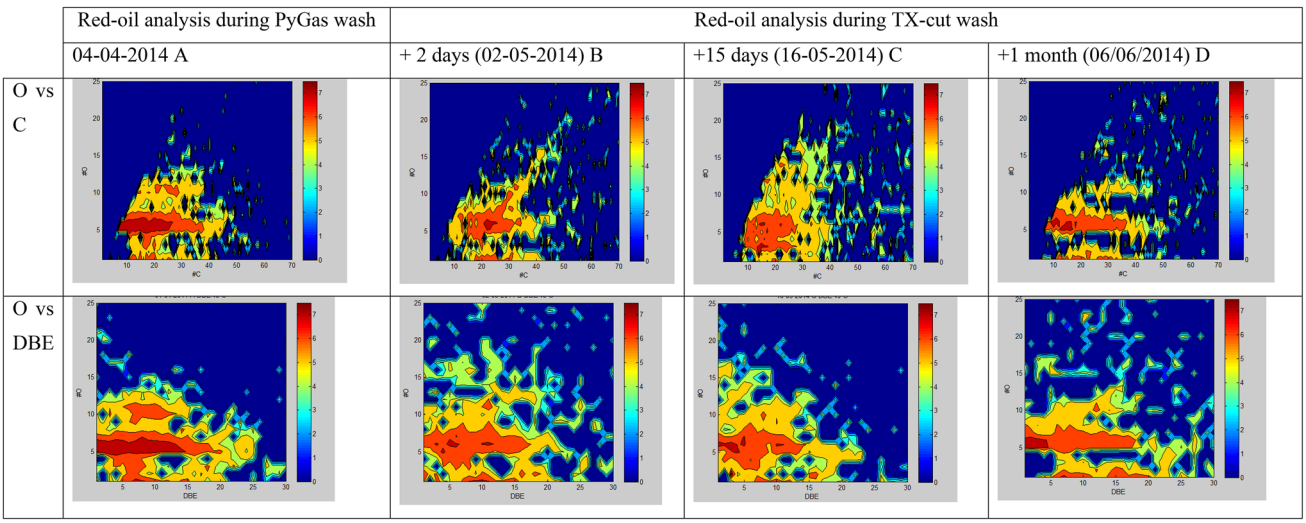

Fig. 4 Contour plots in a logarithmic scale obtained after acquisition on UPLC-QTOF of the different red-oil samples (*DBE* double bond equivalent)

Table 2 Demulsification experiments using PW/PyGas after red-oils addition obtained with TX-cut wash and with Pygas wash

	Blank	Red-oil (1.5 vol%) from TX-cut	Red-oil (1.5 vol%) from PyGas
Turbidity (NTU)	146 ± 4	163 ± 4	185 ± 5
% Average increase turbidity	–	9 %	20 %

contributing factors to emulsions in quench water systems and other factors may also affect emulsion stability; including types of feedstock and other recycle streams.

Conclusion

As illustrated by the contour plots from UPLC-QTOF, this study successfully showed that the nature of the aromatic wash (PyGas vs TX-cut) applied to the caustic tower greatly influences the red-oil structures and their concentration. Reactive monomers such as styrene, CPD or indene present in PyGas can easily react with the polyaldols to form aromatic/conjugated oxygenate. Additionally, this study proved that the PyGas wash altered the red-oils structure which led to species having stronger emulsification properties than the red-oils coming from TX-cut wash, most probably because of the generation of these new oxygenated species mentioned above. It is therefore recommended to perform caustic tower washes with an aromatic solvent which contains little to no reactive compounds (such as TX-cut). Alternatively, it is recommended to reroute the red-oil stream downstream the QWT to avoid emulsification issues. Finally, it was shown that the in-house UPLC-QTOF method that has been developed is perfectly adapted to analyze complex samples with hydrocarbons compounds containing multiple oxygens such as red-oils species.

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